LIBRARY

MAR 25 1925

Technical Paper 352

DEPARTMENT OF THE INTERIOR
HUBERT WORK, SECRETARY
BUREAU OF MINES
H. FOSTER BAIN, DIRECTOR

DETECTION OF SMALL QUANTITIES OF PETROLEUM VAPOR WITH THE BURRELL METHANE INDICATOR

BY

G. W. JONES and W. P. YANT

WASHINGTON
GOVERNMENT PRINTING OFFICE
1924

Generated on 2024-10-06 16:22 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google

Digitized by Google

Original from
UNIVERSITY OF MICHIGAN

U. S. Govt.
9t
2-25-1924

The Bureau of Mines in carrying out one of the provisions of its organic act—to disseminate information concerning investigations made—prints a limited free edition of each of its publications.

When this edition is exhausted copies may be obtained at cost price only through the Superintendent of Documents, Government Printing Office, Washington, D. C.

The Superintendent of Documents *is not an official of the Bureau of Mines.* His is an entirely separate office and he should be addressed:

SUPERINTENDENT OF DOCUMENTS,
Government Printing Office,
Washington, D. C.

The general law under which publications are distributed prohibits the giving of more than one copy of a publication to one person. The price of this publication is 5 cents.

II

First edition, October, 1924

Generated on 2024-10-06 16:20 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

CONTENTS

	Page
Introduction	1
Composition of petroleum vapors	2
Combustion of petroleum vapors	5
Flammable or explosive limits of petroleum vapor	7
Petroleum-vapor scale tests	9
Derivation of scale from tests	12
Description of Burrell indicator	14
Instructions for operation	14
Procedure for testing with the Burrell indicator	16
Accessible places	16
Inaccessible places	16
Summary	18
Publications on petroleum vapors	19

TABLES

TABLE 1.	Percentage and average carbon content of petroleum vapors from different places about petroleum refineries	3
2.	Combustion data of the hydrocarbon gases existing in petroleum vapors	6
3.	Summarized results of tests showing average and maximum variations found in using the Burrell indicator for the determining of petroleum vapor	11

ILLUSTRATIONS

PLATE I.	Making a test with the Burrell methane indicator	16
FIGURE 1.	Curve showing percentage indication on the methane scale when different amounts of petroleum vapors were tested	10
2.	Petroleum-vapor scale for Burrell gas indicator	12
3.	Detail drawing of Burrell indicator	13
4.	Attachment to indicator for sampling petroleum vapors from inaccessible places	17

Generated on 2024-10-06 16:25 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

DETECTION OF SMALL QUANTITIES OF PETROLEUM VAPOR WITH THE BURRELL METHANE INDICATOR

By G. W. Jones and W. P. Yant

INTRODUCTION

For the determination of small quantities of petroleum vapors a simple portable device is needed which can be easily manipulated by workmen not skilled in the use of chemical apparatus. It should be accurate enough to warn them of an atmosphere that may be dangerous—either explosive or asphyxiating.

The Burrell methane indicator developed at the Pittsburgh experiment station of the Bureau of Mines,[1] designed for detecting methane in mines, can be used as well for detecting other combustible gases or vapors.

For this report data have been collected showing the composition and percentages of the vapors that may be given off by crude petroleum and its products. These data give the average composition of the vapors that may be encountered, and a scale has been devised for the indicator from tests with vapors of a composition given by the above data.

As the title indicates, the apparatus is limited to the detection of small quantities of petroleum vapors. Some crude oils, especially some of the Mexican crudes refined in the United States, give off rather high percentages of hydrogen sulphide, especially during distillation, which in itself is a great deal more toxic[2] than petroleum vapors. Obviously the values that this report gives for the limit of safe concentrations of petroleum vapor do not necessarily mean that an atmosphere is safe to breathe. If hydrogen-sulphide gas or other toxic gases are present, special tests for these must be provided. If hydrogen sulphide is suspected, its presence can be ascertained by moistening filter papers with a 5 per cent, by weight, solution of lead acetate and lowering the paper into the tank or container to be

[1] Burrell, G. A., Description of a portable gas detector; Jour. Ind. and Eng. Chem., vol. 8, 1916, p. 365. Milligan, L. H., A critical study of the Burrell indicator for combustible gases in air: Tech. Paper 357, Bureau of Mines, 1924, 40 pp.

[2] Sayers, R. R., Mitchell, C. W., and Yant, W. P., Hydrogen sulphide as an industrial poison. Reports of Investigations, Serial No. 2491, Bureau of Mines, June, 1923.

Generated on 2024-10-06 16:21 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

tested; the presence of hydrogen sulphide is indicated by a darkening of the paper.

A quantitative determination of the hydrogen sulphide can be made by use of the Tutwiler apparatus [3], which is commonly used for the determination of hydrogen sulphide in gases to be used for heating and lighting.

Men should not be allowed to work longer than an hour or two in atmospheres containing as much as 0.01 per cent hydrogen sulphide, nor allowed under any consideration to enter tanks without respiratory protection if the atmosphere contains 0.05 per cent.

The odor of this gas is not to be trusted as an indication, for the sense of smell becomes temporarily paralyzed soon after exposure, and a false sense of security results.

Should the filter paper be darkened after five minutes' exposure, or should a Tutwiler analysis exceed the limits given, the tank or chamber should be thoroughly steamed or aired until the test gives negative results. The general procedure for using the indicator, as given to this report, can then be followed.

COMPOSITION OF PETROLEUM VAPORS

Table 1 shows the predominating hydrocarbon content and the percentages of gases and vapors liberated by petroleum and its products from storage tanks, tankers, and similar places. The table gives the average number of carbon atoms per molecule in the gas or vapor, although other hydrocarbons than the ones given may be present. For example, the first sample in the table indicates four carbon atoms to the molecule, or butane. This was the average composition given by the analysis. Separation of this gas into its different constituents would have revealed the presence of ethane, propane, pentane, and perhaps other hydrocarbon vapors as well. In this report the paraffin hydrocarbons from ethane to butane, inclusive, are considered as gases and those from petane upward as vapors.

[3] Gas Chemists' Hand Book, American Gas Association, 2d ed., 1922, pp. 332–336.

Generated on 2024-10-06 16:23 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Generated on 2024-10-06 16:19 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google

TABLE 1.—*Percentage and average carbon content of petroleum vapors taken from different places about petroleum refineries*

Source and description	Average molecular carbon content of petroleum vapor								Petroleum vapor, per cent	Remarks
	1	2	3	4	5	6	7	8		
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	.....		
Heavy Mexican crude-oil storage tank				4.0					3.5	Explosive.
Do				4.2					3.4	Do.
Do				4.3					1.8	Do.
Light Mexican crude oil storage tanks:										
Sampled 6 feet above oil				3.9					5.8	Do.
Receiving oil from tanker (sampled 10 feet above oil)				4.0					5.2	Do.
Do				4.4					5.3	Do.
				4.3					5.3	Do.
				4.0					4.7	Do.
			3.4						4.9	Do.
Sampled just above oil				3.8					3.5	Do.
Sampled 15 feet above oil				3.9					6.0	Do.
Sampled 5 feet above oil				4.2					6.4	Do.
Sampled above oil				3.7					4.0	Do.
Sampled 1 foot above oil				4.0					2.8	Do.
Mid-Continent crude-oil storage tanks:										
Sampled 8 feet above oil				3.8					3.7	Do.
Sampled 1 foot above oil				4.0					5.2	Do.
Do				3.6					5.8	Do.
Do				3.7					4.1	Do.
Crude-naphtha distillate and finished-product tanks:										
Direct from skimming plant		2.1							5.7	Do.
Direct from coke stills (sampled 1 foot above oil; probably cracked).		2.1							26.90	Explosive when diluted with air.
Direct from coke stills		2.5							1.3	Not explosive.
Pressure-still distillate			3.4						10.3	Explosive when diluted with air.
Crude-naphtha storage				3.7					30.4	Do.
Crude heavy naphtha				4.5					1.19	Not explosive.
				3.6					1.61	
Untreated gasoline:				4.1					21.8	Explosive when diluted with air.
Tank nearly full				4.5					22.7	Do.
Little oil in tank and lower manhole open (sampled 2 feet above oil).					5.2				3.5	Explosive.
Little oil in tank and lower manhole open						6.3			3.6	Do.
Finished naphtha:										
Taken from dome of tank car						6.5			4.9	Do.
Do							6.8		4.9	Do.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Generated on 2024-10-06 16:19 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google

TABLE 1.—*Percentage and average carbon content of petroleum vapors taken from different places about petroleum refineries*—Continued

Source and description	Average molecular carbon content of petroleum vapor								Petroleum vapor, per cent	Remarks
	1	2	3	4	5	6	7	8		
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	.....		
Refined gasoline:										
Low-grade gasoline (sampled 6 inches above oil)				4.5					12.0	Explosive when diluted with air.
Low-grade gasoline; some oil (sampled 4 feet above oil)					5.3				3.2	Explosive.
Low-grade gasoline; some oil (sampled 6 feet above oil)				4.3					2.2	Do.
59°–60° B. gasoline (taken from top of tank)					5.5				9.7	Explosive when diluted with air.
Do					5.5				9.6	Do.
Storage tank; finished gasoline (sampled 2 feet under roof)					5.2				3.0	Explosive.
High-grade gasoline (sampled 6 inches above liquid)				4.0					93.4	Explosive when diluted with air.
High-grade gasoline; some oil (sampled 4 feet above liquid)				3.8					90.2	Do.
High-grade gasoline; some oil (sampled at top of tank)				3.9					56.9	Do.
80° B. casing-head gasoline (sampled at top of tank)				4.1					83.6	Do.
Do				4.1					80.4	Do.
Refined kerosene:										
Tank contained 6 inches of oil (sampled at middle of tank)								10.0	.2	Not explosive.
Do								10.0	.1	Do.
Tank contained 6 inches of oil (samples 3 feet above oil)								11.0	.1	Do.
Do								11.2	.1	Do.
Tank had been used for receiving cracked gas oil from crude stills (sampled at side of tank 4 feet above bottom 6 inches above oil).					5.2				3.8	Explosive.
Do					5.3				3.6	Do.
Gas-oil distillate; probably had some naphtha in it; around cracking temperature.		2.4							37.2	Explosive when diluted with air.
Straight-run gas oil			3.6						1.7	Explosive.
Fuel oil direct from coke stills (sampled 2 feet above oil)					5.0				.71	Not explosive
Fuel oil steamed continuously; temperature, 116° F.								10.0	.21	Do.
Test distillate, crude burning oil; similar to kerosene (sampled 6 inches above oil).			3.2						1.25	Do.
Residuals left in tank after steaming and ventilating; tank had been used to receive crude naphtha from crude stills:										
Sampled 4 feet from bottom and 4 feet from side opposite lower manhole.								11.6	.01	Do.
Do								12.0	.01	Do.
Same tank but sampled 10 inches above center of tank							6.7		.80	Do.
Do							6.9		.75	Do.

The temperature at which the above samples were taken varied from about 32° to 100° F. Exact data as to the temperature of each gas when sampled in many cases were not available.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Inspection of the table shows that the predominating gases and vapors range from ethane (C_2H_6) to duodecane ($C_{12}H_{26}$). The amount of combustibles varies from only a trace (0.01 per cent) to 93.4 per cent. The data also show that two types of combustibles are present:

1. Gases of lower molecular weight, such as methane, ethane, propane, and butane dissolved in the crude petroleum and its products. These gases are liberated during the first part of the distillation processes, or during the weathering of petroleum, etc. The proportions of these gases present may range from a trace to a very high percentage.

2. Vapors of higher molecular weight from the liquid distillates. A large majority of the samples analyzed showed vapors of this average composition, and vary from pentane (C_5H_{12}) to duodecane ($C_{12}H_{26}$).

Closer inspection of the table shows that the vapors having 10 or more carbon atoms to the molecule are never present in sufficient quantity to produce explosive mixtures, the highest proportion being 0.21 per cent. The average number of carbon atoms in the molecule must be seven or less in order for the hydrocarbon vapors to have enough vapor pressure to produce explosive mixtures at ordinary temperatures. From the data given in the table, the petroleum vapor scale for the Burrell indicator should give indications on the safety side for the gases and vapors from ethane to heptane, inclusive.

COMBUSTION OF PETROLEUM VAPORS

When hydrocarbon gases are burned in the presence of an excess of oxygen (or air) there is a loss of volume, and for each gas mixture the contraction in volume is proportional to the quantity of that gas originally present. For example, methane completely burned yields carbon dioxide and water vapor, and as the water vapor condenses to liquid water the contraction in volume is as follows:

$$CH_4+2O_2=CO_2+2H_2O$$
Volumes $1+2=1+0$
Contraction $1+2-1=2$

As two volumes of water vapor are formed and carbon dioxide is the only gas left, two volumes of contraction result from the burning of each volume of methane. The Burrell indicator measures the contraction produced and a scale gives the percentage of gas present. For each gas present the amount of contraction is directly proportional to the amount of that gas. For different gases the contraction produced for a given volume of gas varies with the kind of gas.

Combustion data of those petroleum vapors that have sufficient vapor pressures at ordinary temperatures (below 120° F.) to produce explosive mixtures are given in Table 2. The vapors range from ethane to heptane, inclusive.

Generated on 2024-10-06 16:18 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Generated on 2024-10-06 16:24 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google

TABLE 2.—*Combustion data of the hydrocarbon gases existing in petroleum vapors*

1	2	3	4	5	6	7	8	9	10	11	12
Hydrocarbons	Formula	Molecular weight	Chemical reaction when burned with oxygen (air)	Volumes required for complete combustion		Products of combustion per volume of gas burned			Contraction produced when volume of gas is burned	Lower flammable limit	Contraction produced when 100 c. c. of vapor-air mixture at lower flammable limit is burned
				O_2	Air	CO_2	H_2O vapor	N_2			
Methane	CH_4	16.03	$CH_4+2O_2=CO_2+2H_2O$	2.0	9.50	1.0	2.0	7.56	2.0	[b] 5.50	
Ethane	C_2H_6	30.05	$C_2H_6+3\frac{1}{2}O_2=2CO_2+3H_2O$	3.5	16.72	2.0	3.0	13.23	2.5	[a] 3.10	7.75
Propane	C_3H_8	44.06	$C_3H_8+5O_2=3CO_2+4H_2O$	5.0	23.89	3.0	4.0	18.90	3.0	[a] 2.15	6.65
Butane	C_4H_{10}	58.08	$C_4H_{10}+6\frac{1}{2}O_2=4CO_2+5H_2O$	6.5	31.06	4.0	5.0	24.57	3.5	[a] 1.65	5.80
Pentane	C_5H_{12}	72.10	$C_5H_{12}+8O_2=5CO_2+6H_2O$	8.0	38.22	5.0	6.0	30.24	4.0	[c] (1.35)	5.40
Hexane	C_6H_{14}	86.11	$C_6H_{14}+9\frac{1}{2}O_2=6CO_2+7H_2O$	9.5	45.39	6.0	7.0	35.91	4.5	[c] (1.15)	5.10
Heptane	C_7H_{16}	100.13	$C_7H_{16}+11O_2=7CO_2+8H_2O$	11.0	52.56	7.0	8.0	41.58	5.0	[c] (1.00)	4.90
Octane	C_8H_{18}	114.14	$C_8H_{18}+12\frac{1}{2}O_2=8CO_2+9H_2O$	12.5	59.72	8.0	9.0	47.25	5.5	[c] (0.85)	4.75

[a] Burgess, M. J., and Wheeler, R. V., The lower limit o finflammation of mixtures of the paraffin hydrocarbons with air: Jour. Chem. Soc., vol. 99, 1911, pp. 2013–2030.
[b] Burrell, G. A., and Oberfell, G. G., the limits of inflammability of mixtures of methane and air: Technical Paper 119, Bureau of Mines, 1915, p. 25.
[c] Calculated.

Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Column 10 of Table 2 shows the contractions produced by one volume of the different hydrocarbons when burned in an excess of oxygen (air); these values range from 2.5 for ethane to 5 for heptane. That is to say, 1 per cent of heptane produces twice as much contraction as the same percentage of ethane. The calculation of the percentage of combustible gases in a mixture from the contraction resulting by burning the gases may be 100 per cent in error when the composition of the gas varies, as given above. However, the actual percentage of gas present is of secondary importance. The user of the indicator desires to know how explosive, or how close to the explosive limit, the atmosphere is, and whether there are any dangers from the toxic effects of the gases and vapors. A determination of the percentage of the combustible vapor is not of great value unless the explosibility of the gas is known. If the scale is considered with respect to the relative explosibility or flammability of the gases the large errors due to varying contractions of the different gases and vapors are largely compensated, as will be shown later.

FLAMMABLE OR EXPLOSIVE LIMITS OF PETROLEUM VAPOR

In column 11 of Table 2 is given the lower flammable limits of the hydrocarbon gases and vapors that may be found in explosive proportions above crude petroleum and its products. Four of the values have been determined experimentally; the others were calculated on the basis that the lower explosive or flammable limit bears a direct relation to the oxygen required for complete combustion—that is $O_2 \times$lower flammable limit=constant, where O_2 equals the volume of oxygen required to burn completely one volume of gas. White[4] has found this method to be accurate for many different types of vapors, and it should apply equally well to hydrocarbons of the same series as found in petroleum vapors.

Taking the four hydrocarbons whose lower flammable limits have been determined, the constant is obtained for the other hydrocarbons as follows:

Lower flammable limits of certain petroleum vapors

a	b	c	d
Vapor	Volume of oxygen required for combustion	Lower flammable limit	b×c
Methane (CH_4)	2.0	5.50	11.00
Ethane (C_2H_6)	3.5	3.10	10.85
Propane (C_3H_8)	5.0	2.15	10.75
Butane (C_4H_{10})	6.5	1.65	10.70
Average (approximate value)			10.80

[4] White, A. G., Limits for the propagation of flame in vapor-air mixtures: Trans. Chem. Soc., vol. 121, 1922, p. 1244.

Generated on 2024-10-06 16:21 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

Using this constant for calculating the lower flammable limits of the hydrocarbons whose limits have not been determined, the values given in column 11 of Table 2 were obtained. As the table shows, the lower flammable limit decreases as the hydrocarbon gases increase in molecular weight.

For the constituents that may be found in petroleum vapor, the lower flammable limits range from 1 per cent (heptane) to 3.10 (ethane). It requires over three times as much ethane as heptane to produce an explosive mixture. On the other hand, one volume of heptane produces two times the amount of contraction when burned; and if a scale which is based on contractions is constructed with respect to relative explosibility, the two opposing factors largely compensate each other. This fact is more easily explained by reference to column 12 of Table 2, which gives the amount of contraction produced when 100 c. c. of vapor-air mixture at the lower flammable limit is burned.

The contraction produced ranges from 4.90 c. c. for heptane to 7.75 c. c. for ethane. If a petroleum vapor of which the composition is not known is tested with the Burrell indicator and gives a contraction af 4.90 per cent, the mixture would just be explosive if the vapors were heptane; but for any of the other vapors, such as pentane or butane, the mixture would be nonexplosive. If the indication was 6 per cent the mixture would be explosive if the vapors were butane. pentane, hexane, or heptane, and not explosive if the vapors or gases were propane or ethane.

In view of the above facts, the only scale that would safely indicate an explosive mixture of petroleum vapor of unknown composition in air should obviously be based on the gas or vapor producing an explosive mixture with the least contraction.

That it may be safe for all conditions of use, the petroleum-vapor scale has been devised on the basis of heptane. One per cent on the scale has been taken as the lower explosive limit, as given in Table 2. The toxic effects of the petroleum vapors (gasoline) obtained in calibrating the proposed scale showed that these vapors in proportions of 0.3 per cent or more become intoxicating to some people on exposure for 30 minutes or longer; therefore this value is taken as the safety limit. In other words, the mixture does not become explosive until the petroleum vapor is present in quantities over three times the amount that it is permissible to allow a person to enter. This wide factor of safety (300 per cent) more than offsets the errors caused by the variations of the composition of the petroleum vapors.

All of the foregoing discussion has been based on the assumption that an excess of oxygen (air) is present, or that combustible vapors are not present in excess of the proportion permitting complete com-

Generated on 2024-10-06 16:19 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

bustion. When these vapors are present in excess, products of incomplete combustion are formed and the results are not correct. A large excess of vapors will cause an expansion of the gases, and may force some of the water out of the gage glass.

If the mixture is within the upper and lower flammable, or explosive, limit when the current is turned on the oil in the indicator, an explosion will result, often blowing some of the water out of the gage glass. When an attempt is made to burn an explosive mixture no danger results other than a loss of water from the apparatus, and this water is easily replaced.

For a quantitative estimation of petroleum vapor, the percentage present must be below the lower explosive or flammable limit; if the vapors are explosive only a qualitative test can be made, which is shown by the mixture exploding in the indicator, and the detector can not be used for mixtures above the upper explosive or flammable limit or for mixtures deficient in oxygen.

PETROLEUM-VAPOR SCALE TESTS

The petroleum-vapor scale was obtained by preparing synthetic mixtures of petroleum vapors in a closed chamber of approximately 1,000 cubic feet capacity. A gasoline was used, which, when vaporized, gave approximately the analysis for heptane and had the following composition: Carbon, 84.3 per cent; hydrogen, 15.7 per cent. The molecular composition, obtained by dividing by the respective atomic weights of carbon and hydrogen, was:

84.3÷12=7.02 carbon.
15.7÷ 1=15.7 hydrogen.

More than the calculated quantity of gasoline to give a desired concentration was put into the chamber on a shallow pan covered with cotton waste. The outlets in the chamber were closed and the gasoline vaporized by passing a rapid current of air over it by means of a fan. When the gasoline was vaporized, two indicators were taken into the chamber, and several tests of the atmosphere were made. Different operators—sometimes four or more—made tests with each indicator; this was done to obtain information on the instrument and to detect personal errors. Both indicators were supplied with a methane scale, and only the methane readings were taken.

When enough tests had been made at a given concentration, more gasoline was vaporized and the tests were continued in increasing concentrations of vapor until the atmosphere became highly intoxicating to the operators; then the tests were discontinued. A second series of tests were repeated on another day, and the concentrations of gasoline vapor were so chosen as to fall between the concentrations

Generated on 2024-10-06 16:22 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

of the previous series of tests. A third series of tests were made at higher concentrations, and special gas masks for removing gasoline vapor were worn by the operators, because at these concentrations

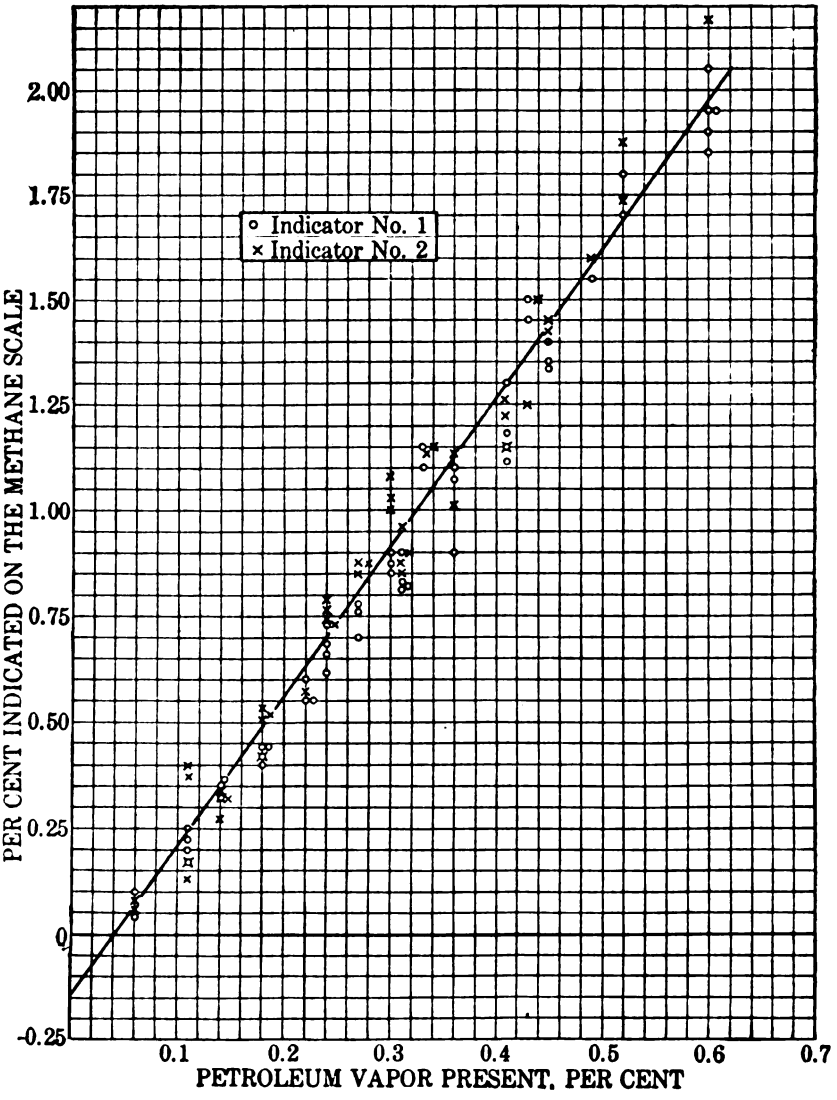

FIG. 1.—Curve showing percentage indicator on the methane scale when different amount of petroleum vapors were tested

(0.60 per cent) the vapors were very intoxicating. The concentrations were not carried above 0.60 per cent, because only 0.30 per cent was found to be intoxicating and it was thought unnecessary to go more than 100 per cent beyond the safety limit.

Generated on 2024-10-06 16:23 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

During each test a sample of the chamber atmosphere was taken by the vacuum-tube method, and an analysis for petroleum-vapor content was made with a Bureau of Mines modified Haldane apparatus.

The percentages indicated on the methane scale are shown on the curve of Figure 1 plotted against the actual percentage of petroleum vapor. The points are seen to fall in an approximately straight line, and the zero mark on the petroleum-vapor scale falls on a point 0.14 per cent below the zero mark of the methane scale.

A straight-line curve of this type can be defined by the following equations:

$$a=sb+c$$

where a=percentage of petroleum vapor present.

s=the slope of the curve, which equals 0.282 in this case.

b=the percentage indication on the methane scale.

c is the constant—that is, the distance intercepted on horizontal axis, which equals 0.04 per cent.

From this equation the percentages of petroleum vapor given in Table 3 were obtained.

TABLE 3.—*Summarized results of tests showing average and maximum variation found in using the Burrell indicator for determining petroleum vapor*

Test No.	Indicators used	Different operators who made tests	Tests made with indicator	Minimum indicated on petroleum-vapor scale, per cent	Maximum indicated on petroleum-vapor scale, per cent	Average indicated on petroleum-vapor scale, per cent [a]	Petroleum-vapor present by Haldane analysis, per cent	Average error, per cent	Maximum error, per cent
1	1	1	4	0.05	0.07	0.06	0.06	0.00	0.01
7	2	5	8	.08	.15	.11	.11	.00	.04
2	2	3	6	.12	.14	.13	.13	.01	.02
8	2	4	8	.15	.19	.17	.18	.01	.03
3	2	3	6	.19	.21	.20	.22	.02	.03
9	2	4	8	.21	.26	.24	.24	.00	.03
4	2	3	6	.24	.29	.27	.27	.00	.03
10	2	4	8	.27	.31	.29	.31	.02	.04
5	2	3	6	.28	.34	.30	.30	.00	.04
6	2	3	4	.35	.36	.36	.33	.03	.03
11	2	3	5	.29	.35	.33	.36	.03	.07
12	2	4	6	.35	.41	.38	.41	.03	.06
15	2	2	4	.38	.46	.44	.43	.01	.05
13	2	3	5	.42	.45	.43	.45	.02	.03
14	2	2	2	.48	.49	.49	.49	.00	.01
16	2	2	4	.52	.57	.53	.52	.01	.05
17	2	2	6	.57	.65	.60	.60	.00	.05
Average								.01	.04

[a] See Table 1, p. 3.

This table gives the summarized results of tests with a vapor approximating heptane. The average percentage variations from the percentages found by Haldane analysis were never greater than 0.03 per cent, and the maximum percentage errors were never greater than 0.07 per cent. The agreement of the results is good, inasmuch as three different series of tests were made on different days, two different indicators were used, and tests were made by six different

Generated on 2024-10-06 16:19 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

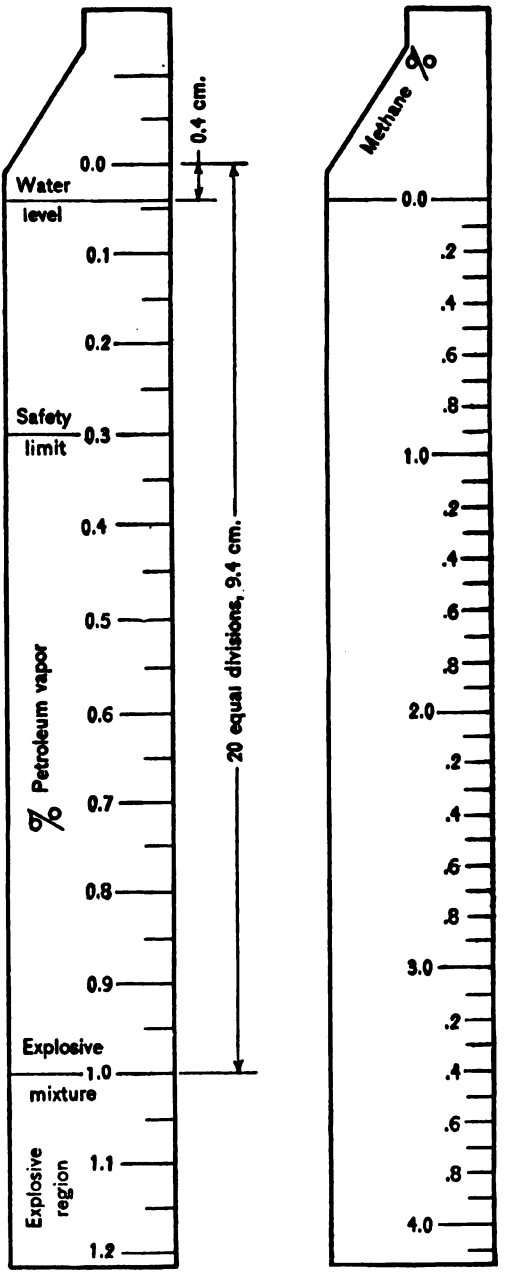

FIG. 2.—Petroleum-vapor scale for Burrell indicator. Combustion period=3 minutes. Gage glass diameter=5.6 mm.

operators, of whom two had never seen or used the indicator before.

Exposure of 30 minutes or longer to an atmosphere containing 0.30 per cent of petroleum vapor had a marked intoxicating effect on one of the operators. All others had symptoms such as mental dullness and loss of equilibrium. Irritation of the eyes was marked when the percentage of petroleum vapor equaled 0.30 per cent.

In view of these physiological effects, a concentration of 0.30 per cent is taken as the safety limit for petroleum vapors. No one should be allowed to remain longer than 30 minutes in a place in which 0.30 per cent is indicated on the petroleum-vapor scale.

DERIVATION OF SCALE FROM TESTS

The petroleum-vapor scale obtained from the methane scale by means of equation 1 is shown in Figure 2. The zero mark is above the water-level mark because of certain variables, such as heat from the glower, solubility of gases in the water, and temperature changes.

Throughout this report the authors have adhered to the term "lower flammable limit" rather than "lower explosive limit," since the Bureau of Mines prefers the former. On the petroleum-vapor

Generated on 2024-10-06 16:24 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

scale, however, the term "explosive limit" is used for the reason that the indicator will be used mainly in refineries by men who are not familiar with the term "flammable limit."

DESCRIPTION OF THE BURRELL INDICATOR

Figure 3 shows a detail drawing of the indicator, which is essentially a metal U tube mounted on a base to keep it upright. The capacity of each of the two branches *g* and *q*, which are connected at the bottom at *x*, is so proportioned as to give the desired scale reading on branch *g*, when the gases are analyzed. The U tube is filled with water to the levels shown, *p* and *r*. The left branch *q* is closed by a cap, *c*, into which is fitted a valve, *b*, for introducing the gases to be analyzed. The upper part *f* of the branch *g* is constricted and made of glass, so that the height of the liquid can be observed when tests are made. Entrance to the glass tube is through connection *e* and rubber tubing *d*. Within the enlarged space of branch *q* is a small platinum wire coil *h*, secured at *n*, which can be heated to a bright red by means of connections to an Edison miner's cap-lamp battery. For observing the platinum coil and obtaining its temperature, a small peephole *s* is provided. Current from the battery is conducted to the indicator through a flexible conductor lead, *t*, securely fastened at *m*. A safety switch, *i*, is provided for turning current on or off the coil *h*, through connections *k* and *l*.

All electrical connections, including the battery, are completely closed and locked, thus avoiding danger from the accidental ignition of gas by sparks.

INSTRUCTIONS FOR OPERATION

The indicator is first filled by unscrewing the cover cap *c*, and pouring in clear, clean, and neutral (preferably distilled) water into the detector until the water level in the gage glass stands at the mark *r*. The bottom of the curved surface of the water in the gage glass should be read.

The perforated protection cap *c* is carefully removed from the platinum glower *h*, and the latter is screwed tightly into its socket, after which the cover cap *c* is replaced and screwed down tight on the jacket. The glower should be in good condition; the turns of the filament should not be distorted and should be evenly spaced.

Make sure that the apparatus is air-tight by closing the valve and blowing into the rubber tube *d*. Pinch the tube while the water level is near the bottom of the gage glass, and hold it for about 15 seconds, after which release it. Give the indicator a few quick shakes from side to side, and if the water level does not rise again to its original

Generated on 2024-10-06 16:24 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

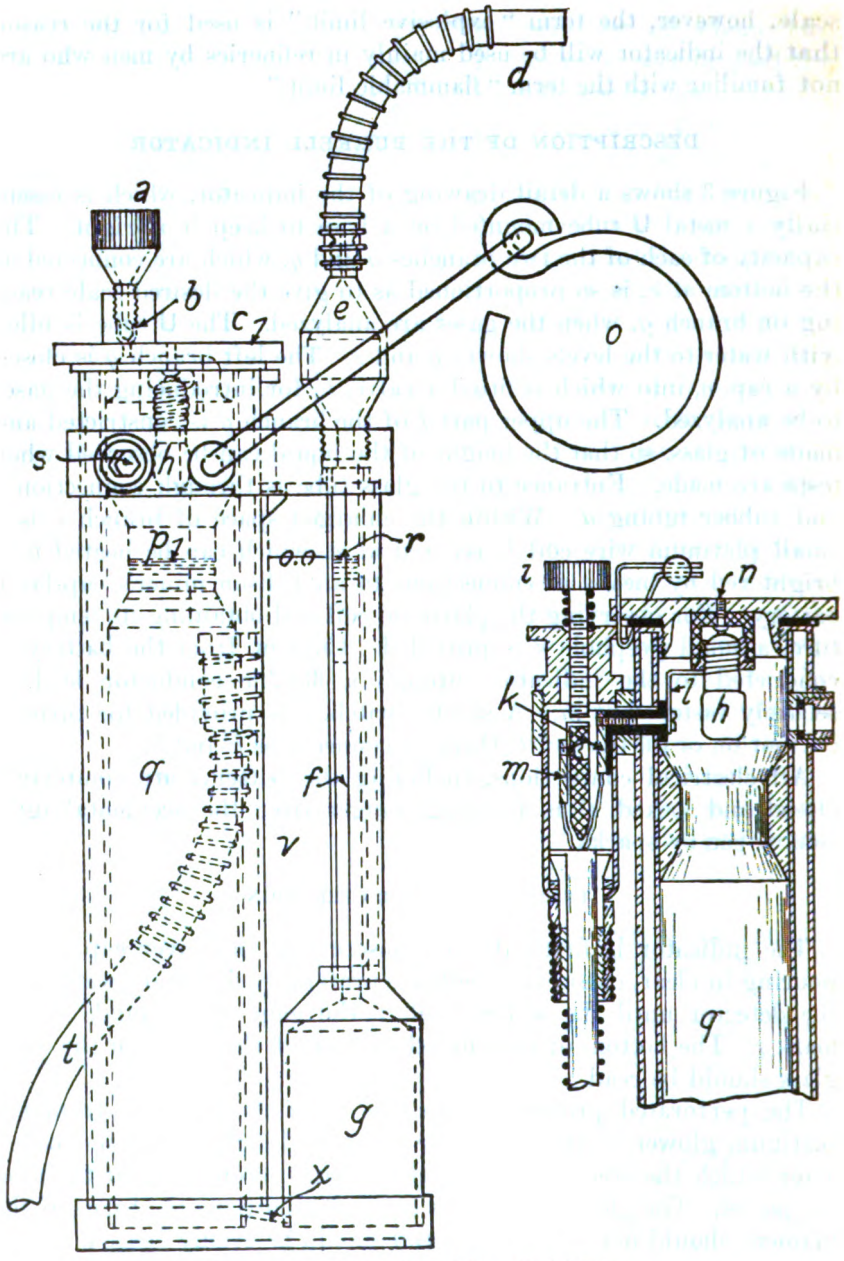

FIG. 3.—Detail drawing of Burrell indicator

position on the scale, the indicator is not tight. In this event, tighten the cap *c* and test again. The indicator must be gas-tight before use.

Attach the indicator to a fully charged battery. To prevent possible burning out of the glower, the battery should not be connected

Generated on 2024-10-06 16:26 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

to the glower until at least two hours after it has been taken off charge. Turn on the current by screwing down contact *i*, and see that the glower heats to a bright red.

When air is blown into tube *d*, and valve *b* is opened two or three turns, water is forced from *g* through the opening at *x* into the larger branch *q*. This causes the water level at *p* to rise until the entire space is filled and water appears in the cup *a*. The cup must not overflow because loss of water will lower the zero mark. Close valve *b* while water remains in the cup, and hold the indicator in the place where the sample is desired. By opening valve *b*, the water falls, comes to its original level, and draws in a sample of gas. Close valve *b*, grasp the handle *o* of the indicator with one hand and hold the bottom of the indicator with the other (see Pl. I, p. 16). Shake the indicator up and down for one minute. Note carefully the position of the water level for any correction that may be necessary to apply to the final reading. Variations of the water level from the zero mark, due to the shaking, must be added or subtracted from the final readings.

Turn on the electric current by turning down the thumbscrew *i* at the back of the instrument, and burn for three minutes. If the glower does not light at once, shake the instrument quickly from side to side to remove water that might be entrapped in it. The glower must be bright red to burn gasoline vapor.

Shut off the current; grasp the handle and base as previously described, and shake the detector up and down for exactly one minute; then give it a gentle side-to-side shake, and read the percentage at once, applying any correction as noted above.

The two shakings bring the gas to the same temperature of the indicator, and saturate the water in the indicator with the gas being anaylzed, so that the possible solubility error is mainly eliminated.

Heat from the glower expands the gases in the combustion chamber, thus depressing the water level and causing the level *r* to rise into *e*. After the current is turned off and the instrument shaken, water mixes with the gas in the combustion space and cools it to the temperature of the indicator. If combustible gas was present in the sample and was burned to water vapor, the contraction in volume of the gas makes the water at *p* rise, and the water level at *r* consequently falls to a point opposite the scale *v* that shows the percentage of vapor originally present in the sample.

To obtain accurate results, the water level in the gage glass must stand at the mark when the indicator is held up by the handle, and *a* and *d* are open. If it does not, the volume of sample taken is not correct. If a drop of water is entrained in the inlet valve, shake

Generated on 2024-10-06 16:21 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

the indicator gently from side to side or even blow gently into the tube *d* and let the water rise again in the gage tube in order to be sure that the valve is open and clear.

The instrument is explosion proof; flames can not get out of the indicator. If an explosive mixture is sampled it explodes, but the only result is that pressure is exerted on the water level *p*, and some of the water is blown out at the tube *d*.

The indicator must not be taken apart in any place containing combustible gas. If trouble develops, go to a safe place before taking it apart.

PROCEDURE FOR TESTING WITH THE BURRELL INDICATOR

ACCESSIBLE PLACES

An exact procedure for all testing with the indicator can not be given; the procedure will necessarily depend upon the type of place to be sampled. For places that have been ventilated and are easily accessible the indicator is connected to the electric battery before the places are entered, and the key to the battery is left behind. When connected to the battery the indicator becomes locked and can not be taken apart except with the special key. This precaution is necessary to prevent the possible production of sparks during tests of atmospheres containing combustible gases. The battery is strapped around the waist while the indicator is held in the hands, as shown in Plate 1. In the atmosphere to be sampled a sample of gas is taken in the manner described. Should this sample show less than 0.3 per cent, the operator should take the next sample a few feet farther ahead, and proceed from one point to another, being sure that the path traveled is safe before he goes farther. When he finds that 0.3 per cent or more of vapor is present, he should retreat and the place should be ventilated or steamed until subsequent tests show less than this safety limit. Before permission is given workmen to enter, tests should be made near the floor, corners, and low places where vapors tend to accumulate.

INACCESSIBLE PLACES

For making determinations of gases in places that can not be entered the attachment shown in Figure 4 is used. The method of making the determination is the same as previously described with the exception of the procedure for taking the samples. The small cup *a* of Figure 3 is removed and the sampling attachment of Figure 4 is put in its place.

To sample the gas a ¼-inch metal pipe is extended into the place to be sampled and the end protruding on the outside connected, as

Generated on 2024-10-06 16:20 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

MAKING A TEST WITH THE BURRELL METHANE INDICATOR

Generated on 2024-10-06 16:21 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

shown, to one arm *b* of the attachment by a short length of rubber tubing. Open valve *e* of the attachment by turning the head *c* and blow into rubber tube on the indicator until the water level reaches

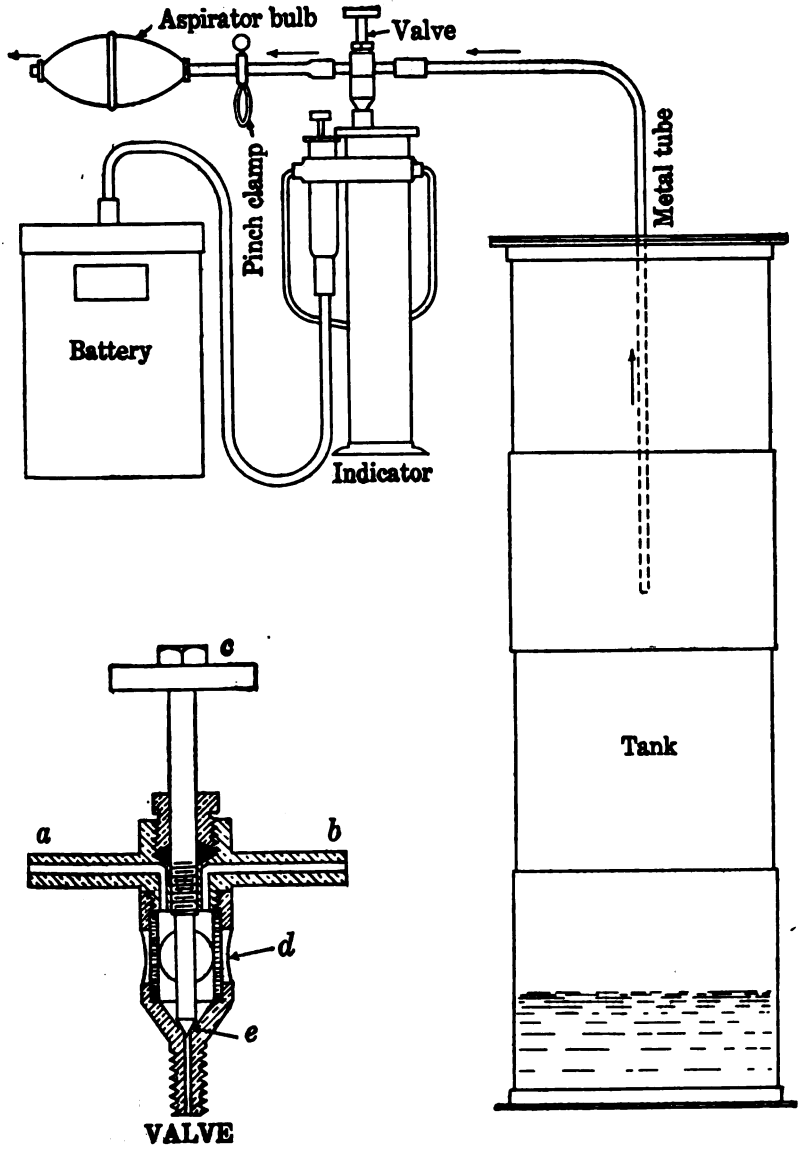

FIG. 4.—Indicator equipped with attachment for sampling gas in a tank or an inaccessible place

and partly fills cup *d*. Then close valve *e*. Compress and release the aspirator bulb connected to *a* at least 50 times to purge all connections of "dead" gas. Close the pinch clamp and open valve *e*,

Generated on 2024-10-06 16:21 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

drawing in a sample of the gas to be tested. Close valve *e* and proceed with the determination as previously described. The aspirator bulb should be tested at frequent intervals to ascertain that its valves are operating properly and that particles of dirt have not lodged in the valve seats.

The accuracy of this method of sampling was determined by preparing a petroleum-vapor mixture in a closed chamber and aspirating the gas through a 20-foot length of both rubber and copper tubing. Tests were also made by taking the indicator directly into the chamber and making determinations. The results obtained are given below:

Comparison of analyses with indicator determinations

Test No.	Kind of tubing	Petroleum vapor found when aspirated through tubing	Petroleum vapor found when tested in the chamber	Petroleum vapor found by Haldane analysis
		Per cent	*Per cent*	*Per cent*
1a	Rubber	0.19	0.29	0.31
1b	do	.16	.34	
1c	do	.21	.31	
	Average	.19	.31	.31
2a	Copper	.34		
2b	do	.30		
2c	do	.32		
	Average	.32	.31	.31

The above table shows that a rubber tube should not be used for sampling petroleum vapors from inclosed places, because a considerable length (here 20 feet) of tubing can absorb a large percentage of the gasoline.

The samples taken through an equal length of copper tubing gave results almost identical with those made directly in the chamber, and also those sampled in vacuum tubes and analyzed with a Bureau of Mines Haldane apparatus, thus showing that the method is suitable for sampling gases from inaccessible places.

SUMMARY

The percentages and predominating hydrocarbon content of the gases and vapors liberated by petroleum and its products while stored in tanks and similar places show that the predominating hydrocarbon gases and vapors range from ethane to duodecane; the percentages present range from only a trace (0.01 per cent) to over 80 per cent. When, however, the vapors are of higher molecular weight than heptane they are not present in quantities suffi-

Generated on 2024-10-06 16:18 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN

cient to produce explosive mixtures at ordinary temperatures (less than 120° F.).

The scale for petroleum vapors devised for use with the Burrell gas indicator is based on the relative explosibility of the vapor, as explosibility is the information most desired.

The 0.3 per cent mark has been chosen as the safety limit because the presence of this proportion of vapor was intoxicating to some of the observers after exposure to it for one-half hour or more.

For testing places that are accessible, the battery used with the indicator is strapped about the waist, the indicator carried in the hand, and tests are made as the user proceeds from place to place. For sampling inaccessible places a small attachment is provided through which the samples of gas are aspirated and introduced into the indicator.

The time required for a test is about four minutes and 20 or more determinations can be made before a freshly charged battery becomes discharged. Actual tests with the indicator in the hands of inexperienced user have shown it will indicate within 0.1 per cent the amount of petroleum vapor present.

PUBLICATIONS ON PETROLEUM VAPORS

A limited supply of the following publications of the Bureau of Mines has been printed. Requests for copies of publications available for free distribution should be addressed to the Director, Bureau of Mines.

The Bureau of Mines issues a list showing all of its publications available for free distribution, as well as those obtainable by purchase at cost from the Superintendent of Documents, Government Printing Office. Interested persons should apply to the Director, Bureau of Mines, for a copy of the latest list.

PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION

TECHNICAL PAPER 117. Quantity of gasoline necessary to produce explosive vapors in sewers, by G. A. Burrell and H. T. Boyd. 1916. 18 pp., 4 figs.

TECHNICAL PAPER 127. Hazards in handling gasoline, by G. A. Burrell. 1915. 12 pp.

TECHNICAL PAPER 272. Permeation of oxygen breathing apparatus by gases and vapors, by A. C. Fieldner, S. H. Katz, and S. P. Kinney. 1921. 24 pp., 4 pls., 3 figs.

TECHNICAL PAPER 348. Gas masks for gasoline and petroleum vapors, by S. H. Katz and J. J. Bloomfield. 1924, 30 pp., 8 pls., 7 figs.

PUBLICATION OBTAINABLE ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS

TECHNICAL PAPER 115. Inflammability of mixtures of gasoline vapor and air, by G. A. Burrell and H. T. Boyd. 1915. 18 pp., 2 figs. 5 cents.

Generated on 2024-10-06 16:25 GMT / https://hdl.handle.net/2027/mdp.39015006902749
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF MICHIGAN